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OCCURENCE AND SEASONAL VARIABILITY OF VOLATILE ORGANIC COMPOUNDS IN SEVEN NEW JERSEY STREAMS

National Water-Quality Assessment Program
Long Island - New Jersey Study Unit

Abstract

Volatile organic compounds (VOC's) were detected in 104 of the 112 samples collected during April 1996-April 1997 from seven streams that drain a variety of land-use settings in New Jersey. A total of 47 different VOC's were detected. The five most frequently detected VOC's were methyl tert-butyl ether (MTBE), in 78 percent of the samples; chloroform, 63 percent; trichloroethene (TCE), 51 percent; 1,1,1-trichloroethane (TCA), 41 percent; and tetrachloroethene (PCE), 35 percent.

Detection frequencies and median concentrations of MTBE, TCE, and PCE were highest at Bound Brook, whose drainage basin has the highest percentage of urban-industrial land use. Detection frequencies and median concentrations of chloroform were highest at the Passaic and Raritan River sites, the sites most affected by discharges from wastewater-treatment plants. The detection frequency and median concentration of TCA were highest at the Saddle River site, whose drainage basin contains primarily urban-residential land.

Detection frequencies and concentrations of MTBE, TCE, and PCE generally were higher in the cooler months (October-March) than in the warmer months (April-September). Median concentrations of MTBE and PCE were consistently higher, at all sites, during the cooler months. Median concentrations of TCE generally were higher in the cooler months. This seasonal pattern may be attributable to the lower volatility and the greater partitioning of these compounds from air to water at cooler temperatures. Higher concentrations of MTBE also may result from increased amounts of MTBE added to gasoline during the winter months in the study area.

Median concentrations of chloroform and TCA generally were higher in the warmer months. Concentrations of chloroform, TCA, and bromodichloromethane decreased significantly with flow at one or more sites, indicating that dilution is likely an important determinant of concentrations of these VOC's.

Contrasting seasonal patterns may indicate different potential sources of VOC's in streams. Higher concentrations in cooler months, when flows are higher, indicate that nonpoint sources may be important in determining the presence and concentration of certain VOC's. Higher concentrations in warmer months, when flows are lower, indicate that point sources or ground-water contributions may be more important than surface runoff in determining the presence and concentration of other VOC's in streams.

Although all VOC concentrations measured met existing water-quality criteria, these criteria have been established for only 26 of the 47 compounds detected. In addition, U.S. Environmental Protection Agency criteria apply only to individual compounds, but most samples contained more than one VOC. The long-term cumulative and synergistic effects of low concentrations of multiple compounds on human and aquatic health are unknown and an area of active research.

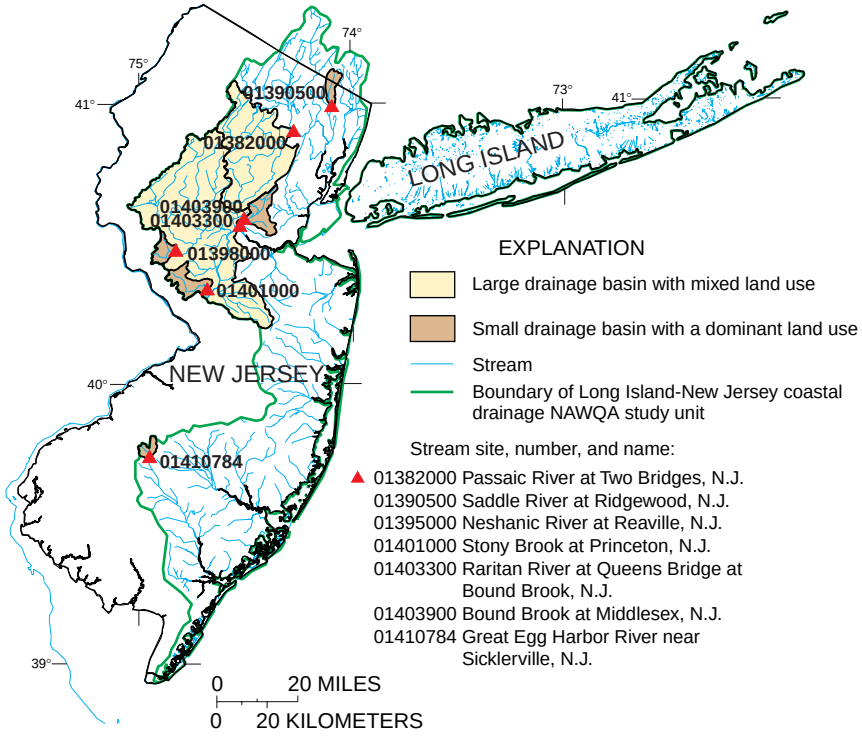

Figure 1. Locations of sites on seven streams sampled for volatile organic compounds from April 1996 through April 1997.

Introduction

Volatile organic compounds (VOC's) are a class of organic compounds found in virtually all natural and synthetic materials. VOC's are present in many household items such as deodorants and perfumes, cleaning and polishing products, paints, adhesives, and ink. VOC's also are used as general anesthetics, to decaffeinate coffee, and in the production of pharmaceuticals and pesticides. Sources of VOC's in surface waters include industrial and municipal wastewater discharges, urban runoff, precipitation, and accidental spills of crude petroleum and fuel products. The presence of VOC's in water is a matter of increasing concern to scientists, industry, and the public because of possible health hazards to humans and aquatic life (Bloemen and Burn, 1993).

The U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) program is designed to assess the status of the Nation's water quality, describe trends in water quality, and provide a sound scientific understanding of the primary natural and human factors that affect the quality of the Nation's water resources. One component of the NAWQA program is the study of the presence, concentrations, and seasonal variability of VOC's in surface water and ground water (Lopes and Price, 1997). Published studies of VOC's in surface water are limited, but results of a recent national study indicate that VOC's are commonly found in urban stormwater (Delzer and others, 1996).

The Long Island-New Jersey coastal drainages study unit, one of 59 areas studied as part of the NAWQA program, includes all of New Jersey, except for those areas that drain to the Delaware and Hudson River Basins, and all of Long Island (fig. 1). The 6,000-square-mile study area is populated by more than 10 million people (U.S. Bureau of the Census, 1991) and includes northeastern New Jersey and western Long Island, two of the most densely populated areas in the United States. Results of previous investigations in the area indicate the widespread occurrence of VOC's in both surface water and ground water (Terracciano and O'Brien, 1997; Stackelberg and others, 1997; O'Brien and others, 1997). Although VOC's were detected in surface water from all land-use settings, detection frequencies and concentrations were highest in water sampled in densely populated urban areas. During these studies, samples were collected annually or infrequently throughout the year; therefore, little is known about the seasonal variability of the presence and concentrations of VOC's in surface water in the study area.

The purpose of this study was to determine the seasonal and spatial variability of the concentrations of VOC's in streams in the Long Island-New Jersey coastal drainages study unit. Results of analyses of 112 stream samples collected from April 1996 through April 1997 at sites on seven streams (fig. 1) that drain a variety of physiographic and land-use settings are presented in this report. Samples were collected during all four seasons at all seven sites.

Selection of Sampling Sites

Seven stream sites were chosen to represent the variety of land uses, physiographic settings, and other drainage-basin characteristics in the study area (table 1). Five sites—Saddle River at Ridgewood, N.J.; Neshanic River at Reaville, N.J.; Stony Brook at Princeton, N.J.; Bound Brook at Middlesex, N.J.; and Great Egg Harbor River near Sicklerville, N.J.—were chosen to represent water-quality conditions in small basins (less than 50 mi^2) associated with specific types of land use and physiography. Saddle River was chosen to represent a drainage basin that consists mostly of suburban residential land. The dominant land use in the Neshanic River drainage basin is agriculture. The Stony Brook Basin is in transition from a predominantly forested and agricultural area to a suburban residential area. Samples were collected more frequently at the Bound Brook and Great Egg Harbor River sites than at the other sites to investigate the effects of urban land use in relatively small drainage basins in the Piedmont and Coastal Plain physiographic provinces, the two major physiographic provinces in the study area. The Piedmont province, which covers most of the northern New Jersey part of the study area, is a broad lowland containing ridges underlain by interbedded sandstone, shale,

Table 1. Drainage basin characteristics and sampling frequency

U.S. Geological Survey site name	U.S. Geological Survey site number	Drainage area (mi^2)	Number of samples collected	Physiographic province	Land use (percent)				Number of point-source discharges	
					Urban					
					Residential	Industrial	Forest	Agriculture	Municipal	Industrial
Passaic River at Two Bridges, N.J.	01382000	361	9	Piedmont, New England	32	15	35	3	22	18
Saddle River at Ridgewood, N.J.	01390500	21.6	11	Piedmont	75	11	11	2	0	2
Neshanic River at Reaville, N.J.	01398000	25.7	9	Piedmont	15	4	27	53	0	0
Stony Brook at Princeton, N.J.	01401000	44.5	12	Piedmont	18	5	46	28	0	0
Raritan River at Queens Bridge at Bound Brook, N.J.	01403300	804	15	Piedmont, New England	19	6	35	30	25	23
Bound Brook at Middlesex, N.J.	01403900	48.4	29	Piedmont	44	24	25	1	0	4
Great Egg Harbor River near Sicklerville, N.J.	01410784	15.1	27	Coastal Plain	24	8	43	1	0	0

conglomerate, basalt, and diabase. The Coastal Plain province, which covers southern New Jersey and Long Island, is mainly flat and is underlain by unconsolidated layers of sand, silt, and clay.

Two sites—Passaic River at Two Bridges, N.J., and Raritan River at Bound Brook, N.J.,—were chosen to represent large drainage areas that integrate the effects of many different types of land uses, physiographic settings, and point-source discharges. No streams on Long Island were chosen for sampling in this study because surface water on the island is not used as a source of public supply, and samples are collected during synoptic studies (Terracciano and O'Brien, 1997).

Field and Laboratory Methods

A VOC sampler designed by the USGS and described in detail by Shelton (1997) was used to collect samples from the stream at the center of flow. Samples were acidified with two drops of 1:1 HCl and shipped on ice to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado, for analysis.

Samples were analyzed at the NWQL for 86 VOC's by using a recently approved method for determination of low concentrations of VOC's in water (Connor and others, 1998). VOC concentrations were determined by purge-and-trap isolation and concentration, and capillary-column gas chromatography/mass spectrometry. This method is based on U.S. Environmental Protection Agency (USEPA) method 524.2, revision 4.0 (U.S. Environmental Protection Agency, 1992), and the method described by Connor and others (1998), with minor improvements and inclusion of strategies for reporting concentrations near the non-detect value (NDV). The NDV, the reporting level for reliable quantitation of VOC's, ranges from 0.05 to 5.0 µg/L (micrograms per liter) for the 86 VOC's measured. Although confirmed detections of the presence of VOC's below these values occurred, accurate quantitation in these instances could not be guaranteed; therefore, such values were given an "E" prefix (for example, E0.02 µg/L). VOC's not detected by the NWQL are reported as less than the NDV (for example, <0.02 µg/L).

Occurrence, Concentration, and Seasonal Variability of Volatile Organic Compounds

VOC's were detected in 104 of the 112 samples collected from April 1996 through April 1997. A total of 47 different VOC's were detected in these samples. Detection frequency and median and maximum concentrations of the compounds detected are listed in table 2, along with USEPA maximum contaminant levels (MCL's) and other water-quality criteria. Data containing an "E" prefix were included in the data set of detected values used for statistical analysis. Non-detect values were not included in the computation of median concentrations. The 39 VOC's not detected in any of the samples are listed in table 3.

The USEPA has established MCL's for drinking water, health advisory levels (HAL's) for lifetime exposure, or freshwater chronic criteria for the protection of aquatic life for only 28 of the 47 compounds detected. All concentrations measured, however, were well within all of these water-quality criteria; MCL's were at least four times the measured concentrations.

Detection Frequency

The 5 VOC's most frequently detected in the 112 samples were methyl tert-butyl ether (MTBE), in 78 percent of the samples; chloroform, 63 percent; trichloroethene (TCE), 51 percent; 1,1,1-trichloroethane (TCA), 41 percent; and tetrachloroethene (PCE), 35 percent. MTBE, chloroform, TCE, and PCE also were among the 6 most frequently detected VOC's in a synoptic sampling at 42 stream sites in New Jersey and Long Island conducted in January 1997 (O'Brien and others, 1998). Chloroform was detected in all samples from the Passaic and Raritan River sites. Both streams have large drainage basins with a large number of point-source discharges (table 1). MTBE was detected in all samples from Bound Brook, a stream whose basin has a high percentage of urban-industrial land. TCA was detected in all samples from Saddle River, a stream whose basin has two point-source discharges and a large percentage of urban-residential land. A sixth VOC, bromodichloromethane, was found in only 24 percent of all samples collected but was detected in all samples from the Passaic River site.

The most frequently detected VOC's at the seven stream sites in the study area are byproducts of and compounds used in gasoline, commercial and industrial processes, and the chlorination of drinking water. MTBE is a fuel oxygenate added to gasoline to enhance combustion, reduce carbon monoxide emissions, and reduce concentrations of the byproduct ozone in the atmosphere. Chloroform and bromodichloromethane are trihalomethanes produced as byproducts of the chlorination of water. Chloroform is also used as an industrial solvent, as an extracting agent, and in the production of fluorocarbons, dyes, and pharmaceuticals. New Jersey is one of six states in which chloroform is produced (Harte and others, 1991). TCE is used extensively as a metal degreaser but also can be found in a wide variety of products including dyes, printing inks, typewriter correction fluid, rug cleaners, and disinfectants. TCE was used in the past as a dry-cleaning solvent, a fumigant, and a general anesthetic and to decaffeinate coffee (Harte and others, 1991). It is no longer used for these purposes because it was found to cause cancer in mice (Budavari and others, 1989). TCA is one of the most commonly used solvents in the United States. It is also used in such products as drain cleaners, shoe polish, spot removers, insecticides, and printing ink. Small amounts are known to leach out of polyvinyl chloride pipes into drinking water (Harte and others, 1991). PCE is used for dry cleaning, in the production of chlorofluorocarbons, and in spot removers, degreasers, paint strippers, and rug cleaners (Harte and others, 1991).

Detection frequencies of the most frequently detected VOC's for all samples were compared to detection frequencies of the same compounds for samples collected during cooler months (October-March) and warmer months (April-September). Detection frequencies of all five compounds were higher for samples collected during the cooler months than for samples

Table 2. Volatile organic compounds detected in 112 samples collected from seven streams in New Jersey April 1996 through April 1997

[IUPAC, International Union of Pure and Applied Chemistry; NWQL, U.S. Geological Survey National Water Quality Laboratory; NDV, Non-detect value; MCL, drinking-water maximum contaminant level (U.S. Environmental Protection Agency, 1996); HAL, health-advisory level, 70-kilogram adult, lifetime (U.S. Environmental Protection Agency, 1996); USEPA, United States freshwater water quality chronic criteria (U.S. Environmental Protection Agency, 1995); CAN, Canadian water-quality guidelines (Canadian Council of Resource and Environment Ministers, 1996); µg/L, micrograms per liter;---, criteria do not exist; E, estimated value; N/A, not available; Bold face, one of the five most frequently detected compounds]

Compound name (IUPAC/NWQL)	Trade name	NDV (µg/L)	Rank	Detection frequency, in percent (number of detections)	Median of detected concentrations (µg/L)	Maximum concentration (µg/L)	Site of maximum concentration (fig. 1)	MCL or HAL (µg/L)	Freshwater chronic criteria for aquatic life (µg/L)
(1-Methylethyl)benzene	Isopropylbenzene	0.20	38	1.8 (2)	0.006E	0.006E	01403900	---	---
1,1,1-Trichloroethane	**Methylchloroform, TCA**	0.05	4	41. (46)	0.02E	1.3	01403900	MCL 200	---
1,1,2-Trichloro-1,2,2-trifluoroethane/Freon 113	Freon 113, CFC 113	0.05	30.5	3.6 (4)	0.01E	0.01E	01403900	---	---
1,1-Dichloroethane	Ethylidene dichloride	0.05	33	2.7 (3)	0.01E	0.05	01382000	---	---
1,1-Dichloroethene	Vinylidene chloride	0.10	23.5	7.1 (8)	0.01E	0.03E	01390500 01403900	MCL7.0	---
1,2,3,4-Tetramethylbenzene/Prer-nitene	Prer-nitene	0.05	38	1.8 (2)	N/A	0.03E	01403900	---	---
1,2,3,5-Tetramethylbenzene/Isodurence	Isodurence	0.05	38	1.8 (2)	N/A	0.02E	01403900	---	---
1,2,3-Trimethylbenzene	1,2,3-Trimethylbenzene	0.05	38	1.8 (2)	N/A	0.04E	01403900	---	---
1,2,4-Trichlorobenzene	N/A	0.20	38	1.8 (2)	N/A	0.01E	01403300	MCL70	CAN 0.5
1,2,4-Trimethylbenzene	Pseudocumene	0.05	16	14. (16)	0.02E	0.10	01398000	---	---
1,2-Dichlorobenzene	o-Dichlorobenzene, 1,2-DCB	0.05	22	8.0 (9)	0.02E	0.06	01403300	MCL 600	CAN 2.5 USEPA 763
1,2-Dimethylbenzene/o-Xylene	o-Xylene	0.05	18.5	12. (13)	0.01E	0.35	01403900	MCL 10,000	---
1,3 and 1,4-Dimethylbenzene/m- and p-xylene	meta and para-Xylene	0.05	13.5	17. (19)	0.03E	0.67	01403900	---	---
1,3,5-Trimethylbenzene	Mesitylene	0.05	38	1.8 (2)	N/A	0.03E	01403900	---	---
1,3-Dichlorobenzene	m-Dichlorobenzene	0.05	27.5	4.5 (5)	0.01E	0.02E	01403300	HAL 600	CAN 25 USEPA 763
1,4-Dichlorobenzene	p-Dichlorobenzene, 1,4-DCB	0.05	20.5	9.9 (11)	0.01E	0.01E	01403300 01403900	MCL 75	CAN 4.0
1-Chloro-2-methylbenzene/2-chlorotoluene	o-Chlorotoluene	0.05	45	0.9 (1)	N/A	0.004E	01403300	HAL 100	---
1-Isopropyl-4-methylbenzene/p-Isopropyltoluene	p-Cymen	0.05	27.5	4.5 (5)	0.01E	0.08	01403900	---	---
2-Butanone/Methyl-ethyl ketone	Methyl-ethyl ketone	5.00	25	6.3 (7)	0.5E	1.6E	01403900	---	---
2-Ethyltoluene	2-Ethyl toluene	0.05	38	1.8 (2)	N/A	0.03E	01403900	---	---
4-Methyl-2-pentanone	Methyl isobutyl ketone	5.00	30.5	3.6 (4)	0.1E	0.3E	01403900	---	---
Acetone	Acetone	5.00	10	29. (32)	2.3E	13	01403900	---	---
Benzene	Benzene	0.05	17	12. (14)	0.06	0.39	01403300	MCL 5.0	CAN 300
Bromochloromethane	Bromochloromethane	0.10	45	1.0 (1)	N/A	0.01	01382000	HAL 10	---
Bromodichloromethane	Dichlorobromomethane	0.10	11	24. (27)	0.08E	0.92	01382000	MCL 6.0	---
Carbon disulfide	Carbon disulfide	0.05	9	30. (33)	0.01E	0.08	01403900	---	USEPA 2.0
Chlorobenzene	Monochlorobenzene	0.05	6.5	32. (36)	0.1	0.37	01403900	MCL 100	CAN 15 USEPA 50
Chloroethane	Ethyl chloride	0.10	38	2.0 (2)	N/A	0.05E	01403900	---	USEPA 230,000
Chloromethane/Methyl chloride	Methyl chloride	0.20	12	21. (24)	0.04E	0.58	01382000	HAL 3.0	---
cis-1,2-Dichloroethene	(2)-1,2-Dichloroethene	0.05	6.5	32. (36)	0.05	0.15	01403900	MCL 70	---
Dibromochloromethane	Dibromochloromethane	0.10	18.5	12. (13)	0.09E	0.67	01382000	MCL 100	---
Dichloromethane/Methylene Chloride	Methylene chloride	0.10	15	16. (18)	0.22	1.0	01382000	MCL 5.0	CAN 98
Diethyl ether	Diethyl ether	0.10	30.5	3.6 (4)	0.24	0.72	01403300	---	---
Ethenylbenzene/Styrene	Styrene	0.05	26	5.4 (6)	0.006E	0.01E	01403900	MCL 100	---
Ethylbenzene	Phenylethane	0.05	20.5	9.8 (11)	0.01E	0.09	01403900	MCL 700	CAN 90

Table 2. Volatile organic compounds detected in 112 samples collected from seven streams in New Jersey April 1996 through April 1997--Continued

Compound name (IUPAC/NWQL)	Trade name	NDV (µg/L)	Rank	Detection frequency, in percent (number of detections)	Median of detected concentrations (µg/L)	Maximum concentration (µg/L)	Site of maximum concentration (fig. 1)	MCL or HAL (µg/L)	Freshwater chronic criteria for aquatic life (µg/L)
Iodomethane/Methyl iodide	Methyl iodide	0.05	45	1.0 (1)	N/A	0.01E	01390500	---	---
Methyl tert-butyl ether/Methyl-t-butyl ether	**MTBE**	0.10	1	78. (87)	0.42	4.8	01403900	HAL 20-200	---
Methylbenzene/Toluene	Toluene	0.05	8	30. (34)	0.06	0.3	01398000	MCL 1,000	---
n-Butylbenzene	1-Phenylbutane	0.05	45	0.9 (1)	N/A	0.05	01398000	---	---
n-Propylbenzene	Isocumene	0.05	38	1.8 (2)	N/A	0.01E	01398000 01403900	---	---
Naphthalene	Naphthalene	0.20	23.5	7.1 (8)	0.03E	0.22	01403900	HAL 20	USEPA 620
tert-Amyl methyl ether	TAME	0.10	13.5	17. (19)	0.03E	0.08E	01403300	---	---
Tetrachloroethene	**Perchloroethene, PCE**	0.05	5	35. (39)	0.04E	0.14	01403900	MCL 5.0	CAN 110
Tribromomethane/Bromoform	Bromoform	0.20	30.5	3.6 (4)	0.04E	0.10E	01382000	MCL 40	---
Trichloroethene	**TCE**	0.05	3	51. (57)	0.03E	0.36	01403900	MCL 5.0	CAN 20 USEPA 21,900
Trichlorofluoromethane	CFC-11, Freon 11	0.10	45	1.0 (1)	N/A	0.06E	01403900	HAL 2,000	---
Trichloromethane/Chloroform	**Chloroform**	0.05	**2**	63 (71)	0.05	1.5	01382000	MCL 100	USEPA 1,240

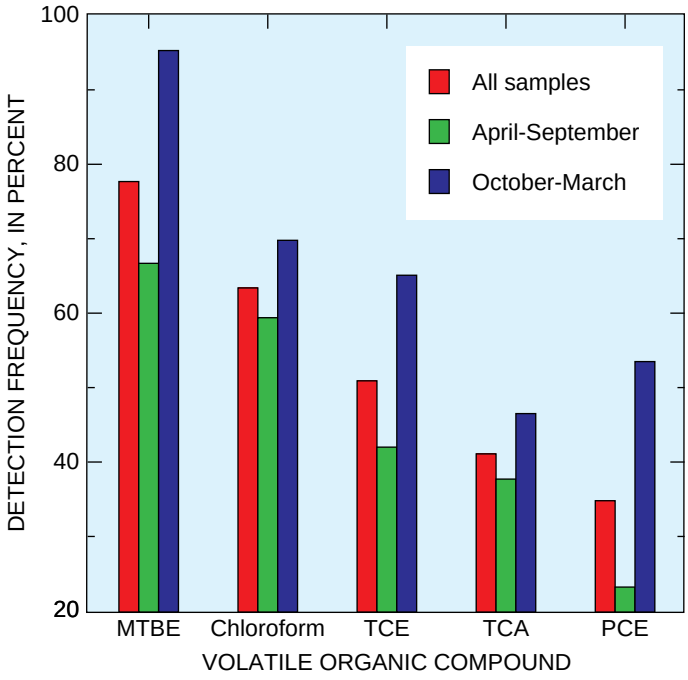

Figure 2. Volatile organic compounds most frequently detected in 112 samples collected during April 1996 - April 1997.

collected during the warmer months (fig. 2) All eight samples in which no VOC's were detected were collected during warm months (May-October).

Seasonal variability in detection frequencies of VOC's was analyzed by comparing results from the cooler period to results from the warmer period at each site (table 4). VOC's detected in at least one sample from each site or in at least 75 percent of the samples for at least one season at one site—13 VOC's—were chosen for comparison. Detection frequencies of MTBE, TCE, PCE, and tert-amyl methyl ether (TAME) were higher during the cooler months than during the warmer months at all sites at which they were detected. The detection frequency was 100 percent during both seasons for four VOC's at the following sites: MTBE at Bound Brook, chloroform at Passaic River and Raritan River, TCA at Saddle River, and bromodichloromethane at Passaic River. Six VOC's—MTBE, chloroform, toluene, carbon disulfide, acetone, and methyl chloride—were detected at least once during the year at each site.

VOC detection frequencies were compared to measured concentrations of the five most frequently detected VOC's at the seven sites (fig. 3). Concentrations of these VOC's were highest at the sites with the highest detection frequencies, with one exception: The detection frequency and median concentration of TCA were highest at Saddle River, but the maximum concentration was measured in a sample collected from Bound Brook during a high-flow event. Annual detection frequencies (table 4) and median concentrations (table 5) of the 13 VOC's studied were highest at the same sites, except for carbon disulfide, whose median concentration (0.02 µg/L) was highest at Passaic River and whose detection frequency (47 percent) was highest at Raritan River.

Concentrations

Median concentrations of the VOC's listed in table 5 for all samples with detections were compared among sites. The median MTBE concentration at the Bound Brook site (0.76 µg/L) was 14 percent higher than that at the Raritan River site and at least twice that at any of the other sites. The median chloroform concentration at the Passaic River site (0.58 µg/L) was twice that at the Raritan River site and more than 10 times

Table 3. Volatile organic compounds analyzed for but not detected in 112 samples collected from seven stream sites in New Jersey April 1996 through April 1997

[IUPAC, International Union of Pure and Applied Chemistry; NWQL, National Water Quality Laboratory; NDV, Nondetect value; µg/L, micrograms per liter; N/A, not available]

Compound name (IUPAC/NWQL)	Trade name	NDV (µg/L)
(1-Methylpropyl)benzene/sec-butylbenzene	N/A	0.05
(1,1-Dimethylethyl)benzene/tert-butylbenzene	N/A	0.05
1,1,1,2,2,2-Hexachloroethane/ Hexachloroethane	Hexachloroethane	0.05
1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA	0.05
1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	0.10
1,1,2-Trichloroethane	Vinyl trichloride	0.10
1,1-Dichloropropene	N/A	0.05
1,2,3-Trichlorobenzene	1,2,3-TCB	0.20
1,2,3-Trichloropropane	Allyl trichloride	0.20
1,2-Dibromo-3-chloropropane	DBCP, Nemagon	0.50
1,2-Dibromoethane	EDB, Ethylenedichloride	0.10
1,2-Dichloroethane	Ethylenedichloride	0.05
1,2-Dichloropropane	Propylenedichloride	0.05
1,3-Dichloropropane	Trimethylenedichloride	0.05
1-Chloro-4-methylbenzene/4-Chlorotoluene	p-Chlorotoluene	0.05
2,2-Dichloropropane	N/A	0.05
2-Hexanone	2-Hexanone	5.00
2-Propenal/Acrolein	Acrolein	2.00
2-Propenenitrile/Acrylonitrile	Acrylonitrile	2.00
3-Chloro-1-propene	3-Chloro-1-propene	0.10
Bromobenzene	Phenyl bromide	0.05
Bromoethene	Vinyl bromide	0.10
Bromomethane	Methyl bromide	0.10
Chloroethene	Vinyl chloride	0.10
cis-1,3-Dichloropropene	N/A	0.10
Dibromomethane	N/A	0.10
Dichlorodifluoromethane	CFC-12, Freon-12	0.20
Ethyl methacrylate	N/A	1.00
Ethyl tert-butyl ether/Ethyl-t- butyl ether	ETBE	0.10
Hexachlorobutadiene	N/A	0.20
Methyl acrylate	N/A	2.00
Methyl acrylonitrile	N/A	2.00
Methyl methacrylate	N/A	1.00
Tetrachloromethane/Carbon tetrachloride	N/A	0.05
Tetrahydrofuran	Tetrahydrofuran	5.00
trans-1,2-Dichloroethene	(E)-1,2-dichloroethene	0.05
trans-1,3-Dichloropropene	N/A	0.10
trans-1,4-Dichloro-2-butene	N/A	5.00
Vinyl acetate	Vinyl acetate	0.05

as high as those at the other five sites. The median concentrations of TCE, PCE, cis-1,2-dichloroethene, and chlorobenzene at the Bound Brook site (0.07, 0.07, 0.06, and 0.2 µg/L, respectively) were more than three times as high as those at the other sites. The median TCA concentration at the Saddle River site (0.09 µg/L) was more than four times as high as those at the other sites. The median concentrations of carbon disulfide (0.02 µg/L) and bromodichloromethane (0.38 µg/L) at the Passaic River site were two and four times as high, respectively, as those at the other sites. The median concentration of TAME at the Raritan River site (0.04 µg/L) was 0.01 µg/L higher than that at the Bound Brook site and 0.03 µg/L higher than that at the Great Egg Harbor River site.

Concentrations of 28 of the 47 VOC's detected were highest in samples from Bound Brook; concentrations of eight compounds were highest in samples from the Passaic River, and

Table 4. Detection frequency of selected volatile organic compounds by sampling site and season

[Light Blue shaded cells= cooler months; Dark Blue shaded cells = warmer months; Bold face indicates detection frequency is greater in warmer months than in cooler months. All volatile organic compounds listed were detected in at least one sample at each site or in at least 75 percent of the samples for at least one season at one site]

Volatile organic compound	Detection frequency (percent)						
	Passaic River	Saddle River	Neshanic River	Stony Brook	Raritan River	Bound Brook	GreatEgg Harbor River
MTBE	100	100	100	100	100	100	80
	83	75	83	25	86	100	29
Chloroform	100	100	**0**	50	100	92	30
	100	50	**33**	50	100	82	24
TCE	67	0	67	0	75	100	60
	17	0	50	0	57	88	35
TCA	**33**	100	0	0	38	83	30
	67	100	0	0	14	53	24
PCE	33	0	0	0	75	100	40
	0	0	0	0	0	65	6
cis-1,2-Di-chloroethene	**33**	0	0	0	50	100	0
	83	0	0	0	14	76	0
Chlorobenzene	**0**	0	0	0	75	92	0
	17	0	0	0	71	76	0
Toluene	33	**0**	67	50	62	50	50
	0	**25**	17	0	29	35	12
Carbon disulfide	33	100	**0**	**0**	50	42	30
	33	0	**17**	**38**	43	29	18
Acetone	**0**	33	33	**0**	**25**	67	40
	17	12	17	**37**	**29**	29	18
Bromodichloro-methane	100	0	0	**0**	**75**	25	0
	100	0	0	**12**	**100**	6	0
Methyl chloride	**0**	33	33	25	38	**8**	**10**
	33	12	17	25	0	**41**	**18**
TAME	0	0	0	0	75	75	10
	0	0	0	0	14	12	0

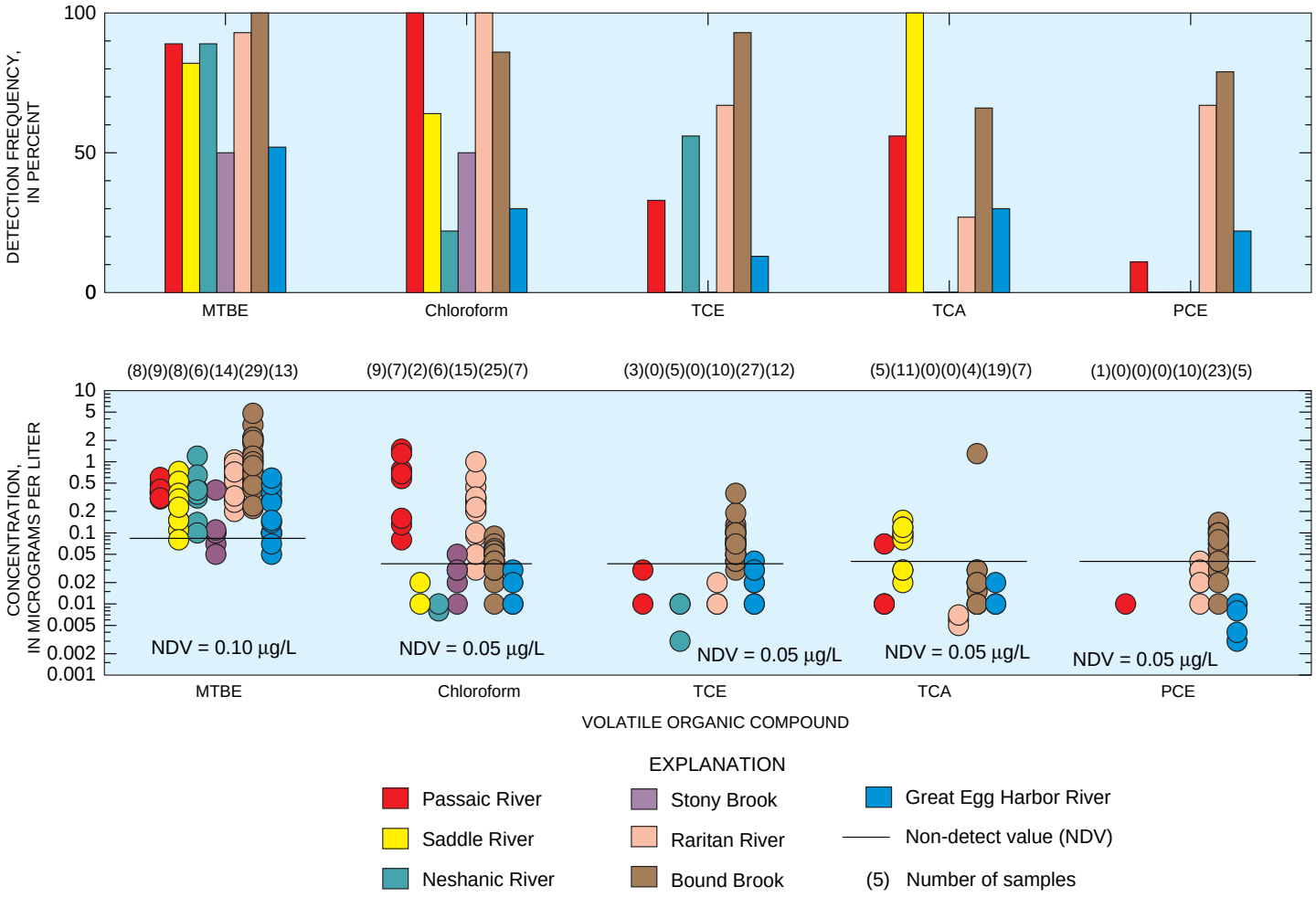

Figure 3. Detection frequencies and concentrations of the most frequently detected volatile organic compounds in the 112 samples collected, by stream site.

concentrations of eight compounds were highest in samples from the Raritan River. Chloroform concentrations measured in all nine samples from the Passaic River site and in 13 of the 15 samples from the Raritan River site were higher than the maximum concentrations detected at the other five sites.

Seasonal variability in concentrations of the five most frequently detected VOC's was examined by plotting the median concentration for the samples collected during the warmer months against that for the samples collected during the cooler months for each site (fig. 4). Seasonal patterns in median concentrations were most evident for MTBE, chloroform, and PCE. At each site, the median concentration of MTBE was greater in the cooler months than in the warmer months. This seasonal pattern may be attributable to the greater volatility of MTBE at warmer temperatures, the greater partitioning of MTBE from air to water at cooler temperatures, and the higher percentage of MTBE used in gasoline during the winter months in the study area (National Science and Technology Council Committee, 1997). The median concentration of PCE also was higher during the cooler months at all three of the sites where PCE was detected. The median concentration of TCE was higher during the cooler months at three of the five sites where TCE was detected.

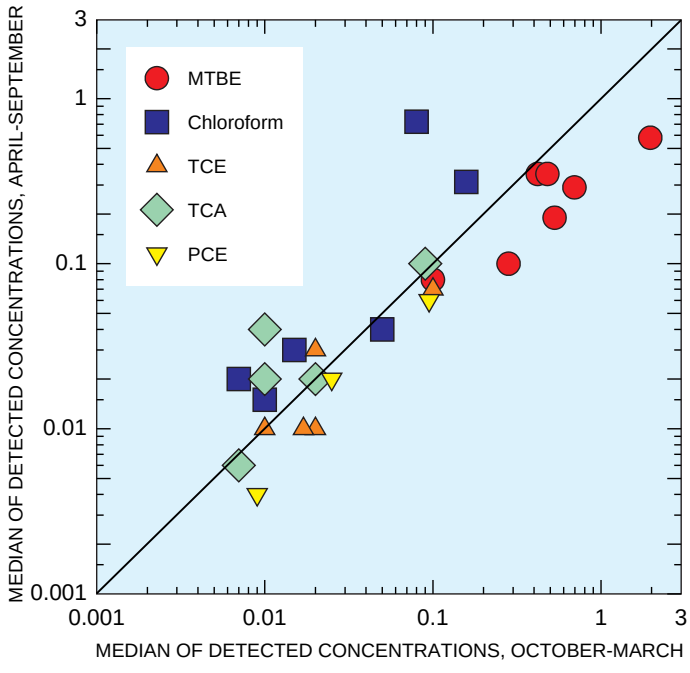

Figure 4. Relation of median warm-season to median cool-season concentrations of volatile organic compounds.

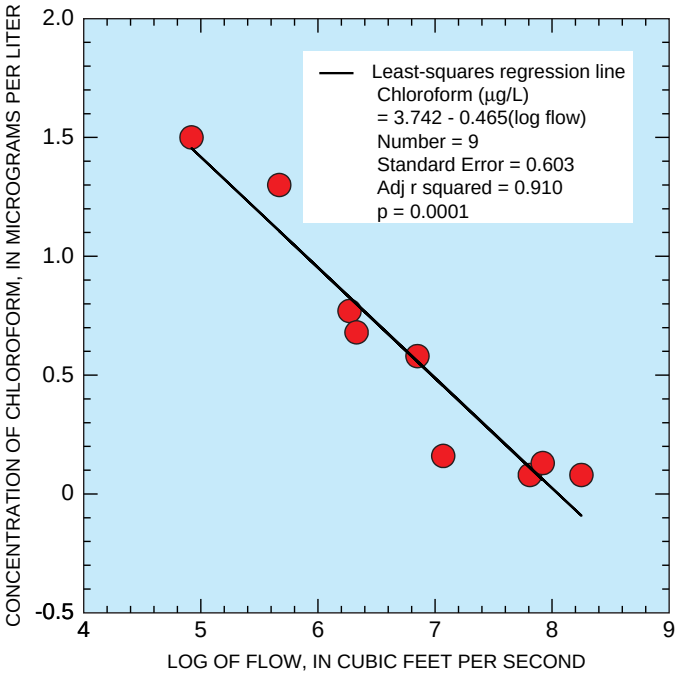

Figure 5. Relation of chloroform concentration to log of flow at Passaic River at Two Bridges, N.J. (site 01382000).

In contrast, the median concentration of chloroform was higher in the warmer months than in the cooler months at six of the seven sites (fig. 4). (No chloroform was detected in samples collected from the Neshanic River site during the cooler months.) This seasonal pattern is likely attributable to a decrease in streamflow during the warmer months, when inputs of chlorinated water from ground-water sources, wastewater-treatment plants (WWTP's), swimming pools, and other outdoor uses of chlorinated public water are less diluted. Consequently, concentrations in streams are higher. An inverse relation was observed between chloroform concentration and flow at the Passaic (fig. 5) and Raritan River sites. The median concentration of TCA also was higher during the warmer months at three of the five sites at which TCA was detected in both seasons (fig. 4)

Concentrations of the five most frequently detected VOC's were examined with respect to streamflow at each of the seven sites, using scatter plots or least-squares linear-regression analysis (Ott, 1988). Least-squares linear regression was used to examine more closely the relation between concentration of VOC and flow at sites at which the VOC was detected in all samples with (100-percent detection frequencies). Concentrations of MTBE were not significantly correlated with flow at any of the sites. Chloroform concentrations, however, decreased significantly with increasing log of flow at the Passaic and Raritan River sites ($p < 0.05$). The most significant ($p < 0.0001$) inverse relation of chloroform concentration to log of flow (adjusted r-squared (r^2 =0.91) was observed at the Passaic River site (fig. 5). The Passaic and Raritan River sites are the only sites receiving chlorinated wastewater discharges (Zripko and Hasan, 1994). Scatter plots showed no correlation between chloroform concentrations and flow at the Bound Brook, Great Egg Harbor River, or Saddle River site. No relation between TCE or PCE concentrations and flow was observed at any of the sites. Concentrations of TCA, however, decreased significantly ($p=0.001$) with log of flow at the Saddle River site ($r^2 = 0.67$), but scatter plots showed no relation between TCA concentration and flow at the other sites. Least-squares linear regression also was used to examine the relation between concentrations of bromodichloromethane and flow at the Passaic River site because it was the only other compound detected in all samples at a site. Concentrations of bromodichloromethane decreased significantly ($p=0.0001$) as log of flow at the Passaic River site increased ($r^2 = 0.905$), but scatter plots indicated no relation at the other sites.

Concentrations of the five most frequently detected VOC's were examined with respect to urban land use in each of the seven drainage basins (fig. 6). The median concentrations of MTBE, TCE, and PCE were highest in Bound Brook, which drains the basin with the highest percentage of urban-industrial land use of the seven sites studied. Median concentrations of MTBE and ranges of concentrations at the other sites were similar and do not appear to be related to the percentage of urban land use in the drainage basins. No relation between percentage of urban land use and median concentration of TCE or PCE was observed at the other sites.

No relation between chloroform concentration and land use was observed (fig. 6). Chloroform concentrations were highest at the Passaic and Raritan River sites. These streams drain the two largest basins. Both the Passaic and Raritan Rivers receive chlorinated wastewater discharges exceeding 50 cubic

Table 5. Median concentration of selected volatile organic compounds by sampling site

[Median concentrations were computed for compounds detected in at least three samples from a site. The volatile organic compounds listed were detected in at least one sample at each site or in at least 75 percent of the samples for at least one season at one site; N/A, not available; Bold face, highest median concentration of each compound]

Volatile organic compound	Median concentration (micrograms per liter)						
	Passaic River	Saddle River	Neshanic River	Stony Brook	Raritan River	Bound Brook	Great Egg Harbor River
MTBE	0.38	0.23	0.38	0.10	0.66	**0.76**	0.15
Chloroform	**0.58**	0.01	0.01	0.03	0.25	0.04	0.01
TCE	0.01	N/A	0.01	N/A	0.01	**0.07**	0.02
TCA	0.01	**0.09**	N/A	N/A	0.01	0.02	0.01
PCE	0.01	N/A	N/A	N/A	0.02	**0.07**	0.01
cis-1,2-Dichloroethene	0.02	N/A	N/A	N/A	0.01	**0.06**	N/A
Chlorobenzene	0.01	N/A	N/A	N/A	0.02	**0.20**	N/A
Toluene	N/A	N/A	0.07	N/A	0.05	0.10	0.04
Carbon disulfide	**0.02**	0.01	0.01	0.01	0.01	0.01	0.01
Acetone	N/A	N/A	N/A	1.90	2.80	**3.40**	1.40
Bromodichloromethane	**0.38**	N/A	N/A	0.01	0.10	0.01	N/A
Methyl chloride	N/A	N/A	N/A	0.03	0.04	**0.06**	0.02
TAME	N/A	N/A	N/A	N/A	**0.04**	0.03	0.01

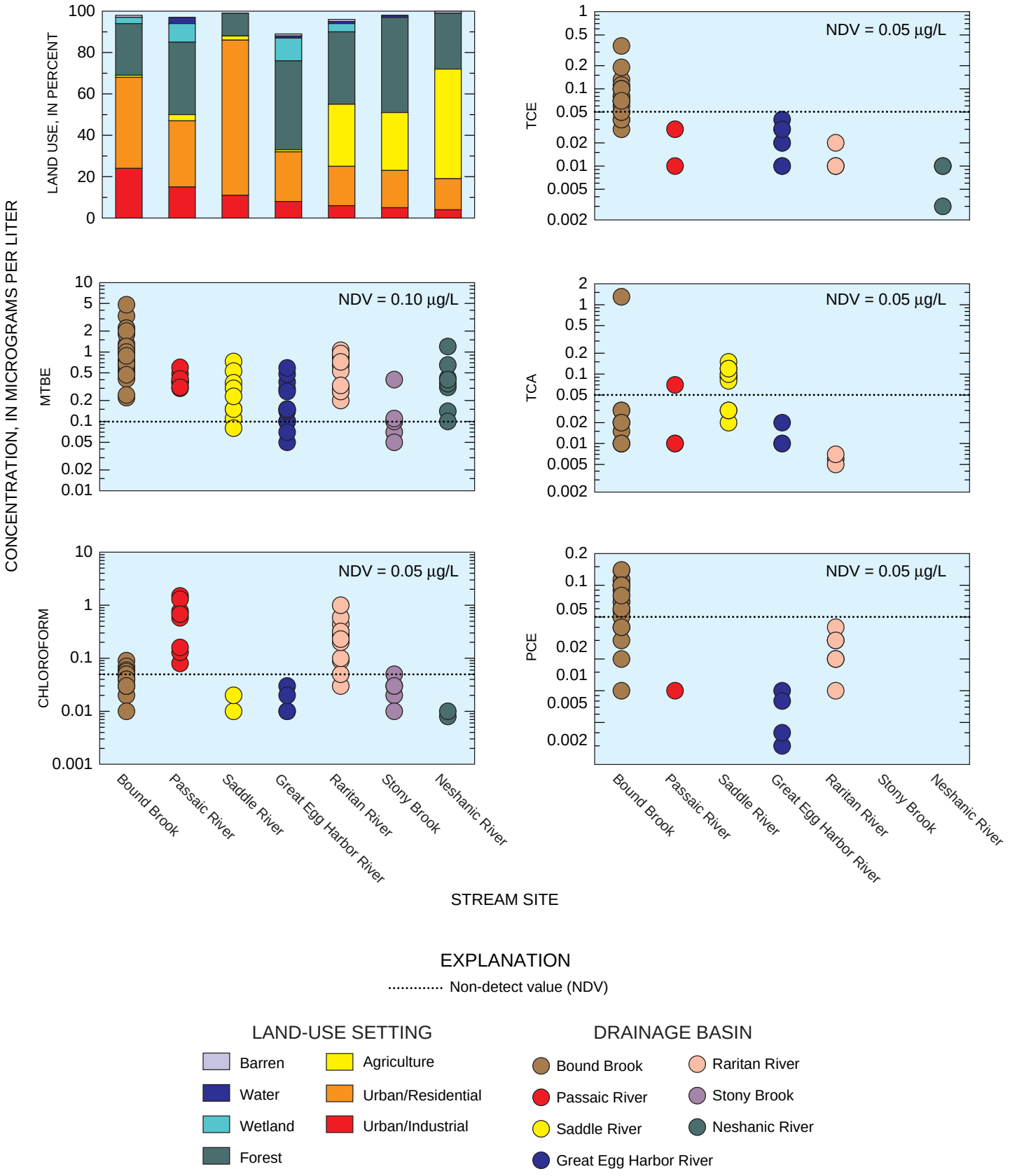

Figure 6. Land-use distribution in the drainage basins of the seven stream sites and concentrations of the five most frequently detected volatile organic compounds in stream samples collected during April 1996-April 1997.

feet per second from WWTP's upstream from the sampling sites (Zripko and Hasan, 1994). No WWTP discharges are present upstream from the five sites at which chloroform concentrations were low.

The range of TCA and TCE concentrations at the sites appears to decrease with the percentage of urban-industrial land use (fig. 6). TCA was not detected at the Stony Brook and Neshanic River sites, the two sites with the lowest percentages of urban-industrial land use. TCE was not detected at the Saddle River or Stony Brook site. The range of PCE concentrations was greatest at the Bound Brook site but did not vary with land use at the other sites. PCE was not detected at the Saddle River, Stony Brook, or Neshanic River site.

Summary and Conclusions

VOC's were detected in 104 of the 112 samples collected at seven streams from April 1996 through April 1997. A total of 47 different VOC's were found in these samples. The five most frequently detected VOC's were MTBE (in 78 percent of the samples), chloroform (63 percent), TCE (51 percent), TCA (41 percent), and PCE (35 percent).

Detection frequencies and median concentrations of MTBE, TCE, and PCE were highest at Bound Brook, whose drainage basin has the highest percentage of urban-industrial land use. Detection frequencies and median concentrations of chloroform were highest at the Passaic and Raritan River sites, the sites most affected by WWTP discharges. The detection frequency and median concentration of TCA were highest at the Saddle River site, whose drainage basin is occupied primarily by urban-residential land use.

Detection frequencies and concentrations of the five most frequently detected VOC's generally were higher in the cooler months (October-March) than in the warmer months (April-September). All eight samples in which no VOC's were detected were collected during May-August. Median concentrations of MTBE and PCE were consistently higher, at all sites, during the cooler months. Median concentrations of TCE generally were higher in the cooler months. This seasonal pattern may be attributable to the lower volatility and the greater partioning of these compounds from air to water at cooler temperatures. Higher concentrations of MTBE also may result from the increased amounts of MTBE added to gasoline during the winter months in the study area.

Median concentrations of chloroform and TCA generally were higher in the warmer months. Concentrations of chloroform, TCA, and bromodichloromethane were found to decrease significantly with flow at one or more sites, indicating that dilution is likely an important determinant of concentrations of these VOC's.

Contrasting seasonal patterns may indicate different potential sources of VOC's in streams. Higher concentrations in cooler months, when streamflows are higher, indicate that nonpoint sources may be important in determining the presence and concentration of certain VOC's. Higher concentrations in warmer months, when streamflows are lower, indicate that point sources or ground-water contributions may be more important than surface runoff in determining the presence and concentration of other VOC's in streams.

Although all VOC concentrations measured met existing water-quality criteria, MCL's, HAL's, or criteria for aquatic life have been established for only 26 of the 47 compounds detected. In addition, USEPA criteria apply only to individual compounds, but most samples contained more than one VOC. The long-term cumulative and synergistic effects of low concentrations of multiple compounds on human and aquatic health is an area of active research.

---Robert G. Reiser and Anne K. O'Brien

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